Prediction of Critical Pressure of Dilute Multicomponent Mixtures

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The properties of dilute mixtures play an important role in many applications. For example, in supercritical extraction, knowledge of the critical point of the system of solvent and extracted material is very useful, in order to determine the conditions at which the solubility change is the maximum.

Gualtieri et al. (1982) proposed a general framework for calculating the critical properties of dilute mixtures. They proposed a procedure that used the van der Waals (vdW) equation of state to obtain an analytical expression for the critical properties. Morrison and Kincaid (1984) pointed out that the agreement between the theoretical results of Gualtieri et al. (1982) (dilute-vdW) and the experimental results was only qualitative. Anselme and Teja (1990) used the framework of Gualtieri et al. (1982) with the Soave-Redlich-Kwong (SRK) equation of state to obtain the expression of the critical properties of dilute mixtures. The results of Anselme and Teja (1990) are better than those obtained by the dilute-vdW method. However, the method of Anselme and Teja (1990) cannot predict properties: it needs some binary interaction parameters that are regressed from the experimental results.

According to Reid et al. (1987), the dependence of the critical pressure of the mixture P_c on mole fraction is often nonlinear. The estimation of P_c is often unreliable compared with that of the critical temperature T_c and the critical volume V_c of the mixture.

In this work, a simple method is proposed to predict the critical pressure of a dilute mixture. The method uses only properties of pure components in the mixture. The method is much simpler than other methods proposed in the literature and the results of this work are better.

New Method

Recently, a number of researchers inverted the formula of the existing method, which was proposed for estimation of property A of the substances to calculate another property B of the substance in the formula. For example, Vetere (1989) inverted the Rackett (1970) equation, which was proposed to calculate liquid density to calculate the critical properties of pure substances. Liu and Chen (1995) inverted the Rackett (1970) equation and the Riedel (1954) equation, which was proposed to calculate the heat of vaporization of a liquid at its normal boiling temperature to predict the critical pressure of pure substances. Good results have been obtained by these methods.

A dilute multicomponent mixture is composed of mostly one species, the main component (or solvent), and other components. Therefore, the dilute multicomponent mixture behaves much like the solvent. We can treat the dilute multicomponent mixture as a single pseudo-component. We might then use some procedure for pure substances to estimate the properties of the dilute multicomponent mixture.

In this work, the method of Chen (1965) that was recommended by Reid et al. (1987) is inverted to calculate the critical pressure of dilute mixtures. Here, the method of Chen is chosen because it is very accurate for estimating the heat of vaporization, and it allows the critical pressure P_c to be calculated easily.

For dilute mixtures, the normal boiling temperature T_b can be estimated as follows

$$T_b = \sum_i x_i T_{b,i} \tag{1}$$

where x_i is the mole fraction of component i and $T_{b,i}$ is the normal boiling temperature of component i. This assumption will introduce some inaccuracy. However, it can be seen from the results obtained that when calculating the critical pressure of dilute mixtures, the errors are acceptable.

For a dilute mixture compared with the heat of vaporization, the mixing heat is negligible, and the sensible heats caused by boiling temperature difference between the components can often compensate with each other. If we omit the mixing heat and the sensible heats caused by the boiling temperature difference between the components in the mixture, the heat of vaporization of the dilute mixture H_v at its normal boiling temperature can be calculated by

$$H_v = \sum_i x_i H_{v,i} \tag{2}$$

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where $H_{v,i}$ is the heat of vaporization of component i at its normal boiling temperature. $H_{v,i}$ can be calculated by the method of Chen (1965)

$$H_{v,i} = RT_{b,i}\frac{3.978T_{br,i} - 3.958 + 1.555\ln(P_{c,i}/P_A)}{1.07 - T_{br,i}} \qquad (3)$$

where R is the universal gas constant, $P_{c,i}$ is the critical pressure of component i, P_A is atmosphere pressure, and $T_{br,i}$ is the reduced temperature of component i, $T_{b,i}/T_{c,i}$.

The critical pressure of the mixture P_c can be calculated by inverting the equation of Chen (1965)

$$P_c=\exp\left\{\left[\frac{H_v(1.07-T_{br})}{RT_b} - 3.978T_{br}+3.958\right]\Big/1.555+\ln P_A\right\} \qquad (4)$$

where $T_{br} = T_b/T_c$ is the reduced normal boiling temperature of the mixture, and the critical temperature of the mixture T_c is calculated as follows (Li, 1971)

$$T_c = \sum_i \phi_i T_{c,i} \qquad (5)$$

$$\phi_i = \frac{x_i V_{c,i}}{\sum_i x_i V_{c,i}} \qquad (6)$$

where $V_{c,i}$ is the critical volume of component i.

From the above formulae, it can be seen that only the properties of pure components are needed in the calculation. Because the assumptions of zero enthalpy of mixing and linear dependence of boiling temperature T_b on composition have been made, the proposed method could only be used for the nonpolar or weakly polar systems.

Results and Discussion

The proposed method is tested with 47 groups of mixtures, which are studied by Anselme and Teja (1990). The composition data of these mixtures are listed in Table 1. All the properties of the pure components used in the calculation are cited from Reid et al. (1987). The results of this work and those presented in the literature are listed in Table 2. The literature includes the dilute-SRK method proposed by Anselme and Teja (1990), and a discrete-SRK method based on the SRK equation coupled with the rigorous solution of the Gibbs criteria. The rigorous method was based on the algorithm of Michelsen and Heidemann (1981) in which the Gibbs criteria are solved directly for T_c and V_c of the mixture. The results presented in the literature are all cited from Anselme and Teja (1990). The dilute-vdW approach of Gualtieri et al. (1982) is not included in Table 2, because its errors are very large compared with the other methods.

The relative errors $\Delta_i = (\text{Calc}_i - \text{Exp}_i)/\text{Exp}_i$ of the methods are shown in Figure 1. From Figure 1, it can be seen that the discrete-SRK method generally underevaluates the critical pressure, as does the dilute-SRK method. In contrast with the above work, the proposed method presents no systematic error. The absolute relative errors $|\Delta_i| = |(\text{Calc}_i - \text{Exp}_i)/\text{Exp}_i|$ of both the discrete-SRK method and the dilute-SRK method are generally much larger than those of the new method. For the method proposed in this work, the absolute relative error of only one point is greater than 10%.

Table 1. Compositions of Dilute Mixture Studied*

Mixture No.	Component (mol. %)
1	n-C_1 (91), n-C_2 (5.6), n-C_3 (0.12), N_2 (3.3)
2	n-C_1 (95.9), n-C_2 (2.6), n-C_3 (0.01), N_2 (1.5)
3	n-C_1 (95), n-C_2 (2.6), n-C_3 (0.78), N_2 (1.6)
4	n-C_1 (94.5), n-C_2 (2.6), n-C_3 (0.81), n-C_4 (0.52), N_2 (1.6)
5	n-C_1 (94.3), n-C_2 (2.7), n-C_3 (0.74), n-C_4 (0.49), n-C_5 (0.01), n-C_6 (0.27), N_2 (1.4)
6	CO_2 (97.39), n-C_2 (2.61)
7	CO_2 (90.25), n-C_2 (9.75)
8	CO_2 (98.95), n-C_2 (1.05)
9	CO_2 (98.57), n-C_2 (1.43)
10	CO_2 (97.39), n-C_2 (2.61)
11	CO_2 (97.34), n-C_2 (2.66)
12	CO_2 (97.18), n-C_2 (2.82)
13	CO_2 (96.67), n-C_2 (3.33)
14	CO_2 (96.59), n-C_2 (3.41)
15	CO_2 (96.09), n-C_2 (3.91)
16	CO_2 (95.04), n-C_2 (4.96)
17	CO_2 (90.15), n-C_2 (9.85)
18	CO_2 (97.48), n-C_2 (2.52)
19	CO_2 (91.44), n-C_2 (8.56)
20	CO_2 (97.51), n-C_2 (1.23), n-C_3 (1.26)
21	CO_2 (97.44), n-C_2 (1.93), n-C_3 (0.63)
22	CO_2 (97.51), n-C_2 (0.63), n-C_3 (1.86)
23	CO_2 (97.46), n-C_2 (1.27), n-C_4 (1.27)
24	CO_2 (97.39), n-C_3 (1.32), n-C_4 (1.29)
25	CO_2 (97.50), n-C_2 (0.81), n-C_3 (0.84), n-C_4 (0.85)
26	CO_2 (90.73), n-C_2 (4.82), n-C_3 (4.43)
27	CO_2 (91.15), n-C_2 (4.45), n-C_3 (4.40)
28	CO_2 (91.16), n-C_2 (4.43), n-C_3 (4.41)
29	CO_2 (93.62), n-C_2 (2.82), n-C_3 (3.56), n-C_4 (3.23)
30	n-C_4 (89.8), n-C_6 (10.2)
31	n-C_6 (89.65), n-C_4 (10.35)
32	n-C_4 (87.45), n-C_5 (12.55)
33	n-C_5 (86.01), n-C_4 (13.99)
34	n-C_3 (92.6), n-C_4 (7.4)
35	n-C_3 (91.8), n-C_6 (8.2)
36	n-C_3 (90.9), n-C_7 (9.1)
37	n-C_{10} (90.0), n-C_{12} (10.0)
38	n-C_{12} (90.0), n-C_{10} (10.0)
39	n-C_9 (90.0), n-C_{13} (10.0)
40	n-C_{13} (90.0), n-C_9 (10.0)
41	n-C_6 (90.0), n-C_{13} (10.0)
42	n-C_{13} (90.0), n-C_6 (10.0)
43	n-C_{10} (90.0), n-C_6 (10.0)
44	n-C_4 (94.61), n-C_8 (5.39)
45	n-C_3 (95.9), n-C_8 (4.19)
46	n-C_{14} (90.0), n-C_6 (10.0)
47	n-C_6 (90.0), n-C_{14} (10.0)

*Cited from Anselme and Teja (1990).

The statistical analysis of the methods is shown in Table 3. From Table 3, it can be seen that the dilute-vdW method is not as accurate as the other two methods proposed in the

Table 2. Calculation Results of the Methods*

Mixture No.	P_c, kPa Exp.	Relative Error, % Dilute-SRK	Discrete-SRK	This Work
1	5,341	0.36	−7.25	−6.42
2	4,932	−0.02	−3.37	−3.08
3	5,180	0.56	−6.31	−4.50
4	5,456	4.51	−9.09	−5.61
5	5,578	25.30	−10.18	−2.76
6	7,250	0.33	0.36	0.99
7	6,935	0.53	0.94	3.26
8	7,324	−0.57	−0.66	0.45
9	7,243	0.04	−0.07	1.46
10	7,229	−1.36	−1.45	1.29
11	7,230	−1.42	−1.52	1.26
12	7,200	−1.24	−1.32	1.64
13	7,180	−1.64	−1.70	1.75
14	7,178	−1.73	−1.77	1.77
15	7,158	−2.12	−2.11	1.89
16	7,108	−2.86	−2.67	2.28
17	6,950	−7.41	−5.50	3.01
18	7,336	−4.31	−4.06	−0.16
19	7,663	−19.87	−15.09	−6.20
20	7,256	−0.63	−0.68	2.59
21	7,263	−0.30	−0.30	1.65
22	7,251	−1.02	−1.09	3.42
23	7,279	−1.81	−1.74	5.41
24	7,278	−2.86	−2.80	7.06
25	7,262	−1.60	−1.60	5.15
26	6,937	−2.67	−1.83	8.62
27	7,212	−9.05	−7.06	4.48
28	7,231	−12.63	−9.68	4.22
29	7,128	−9.46	−6.99	−7.01
30	3,878	−2.22	−3.30	−0.44
31	3,187	−2.67	−2.10	−0.63
32	3,782	−0.50	−0.71	0.37
33	3,472	−0.98	−0.86	−0.29
34	4,285	−2.38	−2.73	−0.33
35	4,690	−3.30	−8.98	−1.94
36	5,109	−1.55	−16.60	−3.27
37	2,126	−2.21	−2.30	−1.13
38	1,904	−2.73	−2.68	−2.42
39	2,323	−2.37	−3.49	−1.21
40	1,822	−0.60	−0.27	−0.71
41	3,442	−0.44	−14.32	−2.38
42	1,991	−6.68	−4.52	−0.95
43	2,306	−5.16	−4.12	−0.91
44	4,049	−3.58	−8.10	−0.62
45	4,930	−2.82	−14.12	−2.94
46	1,757	−12.81	−9.56	−17.02
47	3,568	−5.35	−19.82	−5.21

*The results for SRK methods are cited from Anselme and Teja (1990). The experimental data were compiled by Anselme and Teja (1990).

literature. The reason is that it does not use the interaction parameters between the species. Both SRK methods used binary interaction parameter k_{ij}, which was obtained from the work of Galicia-Luna and Perez (1987).

From the above discussion, it can be seen that the proposed method is more accurate than the methods presented in the literature (dilute-vdW of Gualtieri et al., 1982; dilute-SRK and discrete-SRK of Anselme and Teja, 1990). Another advantage of the proposed method is that it is much simpler than the methods presented in the literature.

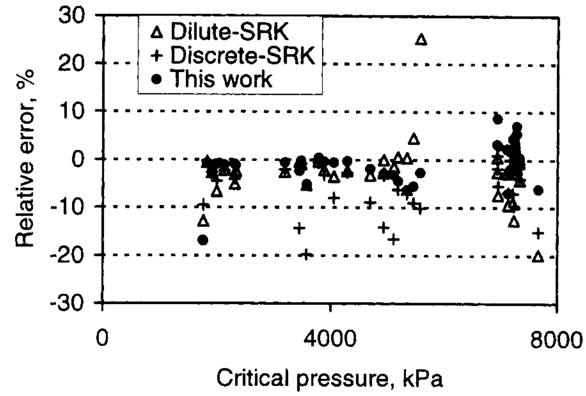

Figure 1. Relative errors of various methods used to calculate critical pressure of dilute multicomponent mixtures.

Table 3. Statistical Analysis of the Methods*

Parameter	Dilute-vdW	Dilute-SRK	Discrete-SRK	This Work
$\lvert\Delta\rvert$, %	28.66	3.76	4.85	3.02
$\bar{\Delta}$, %	31.30	−2.41	−4.79	−0.30
s	34.29	5.84	4.93	4.26

*Results for the literature work are cited from Anselme and Teja (1990).
Relative error: $\Delta_i, \% = 100 \times (\text{Calc}_i - \text{Exp}_i)/\text{Exp}_i$
Average relative error: $\bar{\Delta}, \% = (100/n)\sum(\text{Calc}_i - \text{Exp}_i)/\text{Exp}_i$
Average absolute relative error: $|\bar{\Delta}|, \% = (100/n)\sum|(\text{Calc}_i - \text{Exp}_i)|/\text{Exp}_i$
Standard deviation: $s = \sqrt{\sum(\Delta_i, \% - \bar{\Delta}, \%)^2/(n-1)}$

Conclusion

A simple method is proposed for predicting the critical pressure of dilute multicomponent mixtures from the properties of the pure components. The method inverts the formula of Chen (1965) that was proposed to calculate the heat of vaporization of a liquid at its normal boiling temperature to calculate the critical pressure of dilute multicomponent mixtures. In the calculation, only the properties of pure components are required such as boiling temperature, critical temperature, critical pressure, and critical volume. The results show that the average absolute relative error of the proposed method for the 47 mixtures studied by Anselme and Teja (1990) is 3%, which is smaller than those of the methods presented in the literature and the calculations required are also much simpler.

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